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# Estimating the Heat of Formation of Foodstuffs and Biomass

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## Introduction

Calorie estimates for expressing the energy content of food are common, however they are inadequate for the purpose of estimating the chemically defined heat of formation of foodstuffs for two reasons. First, they assume utilization factors by the body.<sup>1,2,3</sup> Second, they are usually based on average values for their components.

The best way to solve this problem would be to measure the heat of combustion of each material of interest. The heat of formation can then be calculated from the elemental composition and the heats of formation of CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub>. However, heats of combustion are not always available. Sometimes elemental analysis only is available, or in other cases, a breakdown into protein, carbohydrates, and lipids. A simple way is needed to calculate the heat of formation from various sorts of data commonly available.

This report presents improved correlations for relating the heats of combustion and formation to the elemental composition, moisture content, and ash content. The correlations are also able to calculate heats of combustion of carbohydrates, proteins, and lipids individually, including how they depend on elemental composition. The starting point for these correlations are relationships commonly used to estimate the heat of combustion of fossil fuels, and they have been modified slightly to agree better with the ranges of chemical structures found in foodstuffs and biomass.

## Correlations of Heat of Combustion with Elemental Composition

Two correlations of heats of combustion with elemental analysis that are commonly used for fossil fuels are the Boie and Dulong equations. The equations can be presented in various formats, including different units (English or metric) and high or low values based on liquid water or water vapor product. They are presented here for liquid water product in units of J/g.

Boie:

$$-\Delta H_c = 351.5 * \text{wt\% C} + 991 * \text{wt\% H} + 63 * \text{wt\% N} + 105 * \text{wt\% S} - 111 * \text{wt\% O} \quad (1)$$

Dulong:

$$-\Delta H_c = 338.1 * \text{wt\% C} + 1441.8 * \text{wt\% H} + 93.9 * \text{wt\% S} - 180.2 * \text{wt\% O} \quad (2)$$

Muehlbauer and Burnham (1984)<sup>4</sup> determined the heat of combustion of Green River oil shale kerogen by correlating the heat of combustion of the whole shale with organic

carbon content, obtaining a coefficient of 496 kJ/kg shale per wt% organic carbon. Given that kerogen is 80.5% carbon, 10.3% hydrogen, 2.4% nitrogen, 5.75% oxygen, and 1.05% sulfur, Eq. 1 and 2 predict coefficients of 472 and 510 kJ/kg per wt% organic C, respectively.

Similarly, one can use these equations to estimate the heat of combustion of protein, lipids, and carbohydrates,<sup>3</sup> which span the range of elemental compositions in food and biomass. This comparison is shown in Table 1. Carbohydrate and lipid elemental composition were calculated from the chemical structures of starch and a triglyceride. Protein elemental composition was calculated from published amino acid residue analysis of egg, soy, and vetch protein and the chemical formula of the amino acids. Although the Boie and Dulong equations are qualitatively correct, some improvement is obviously necessary. I derived a new correlation by trial and error, and Table 1 shows that it works much better over the entire range of interest:

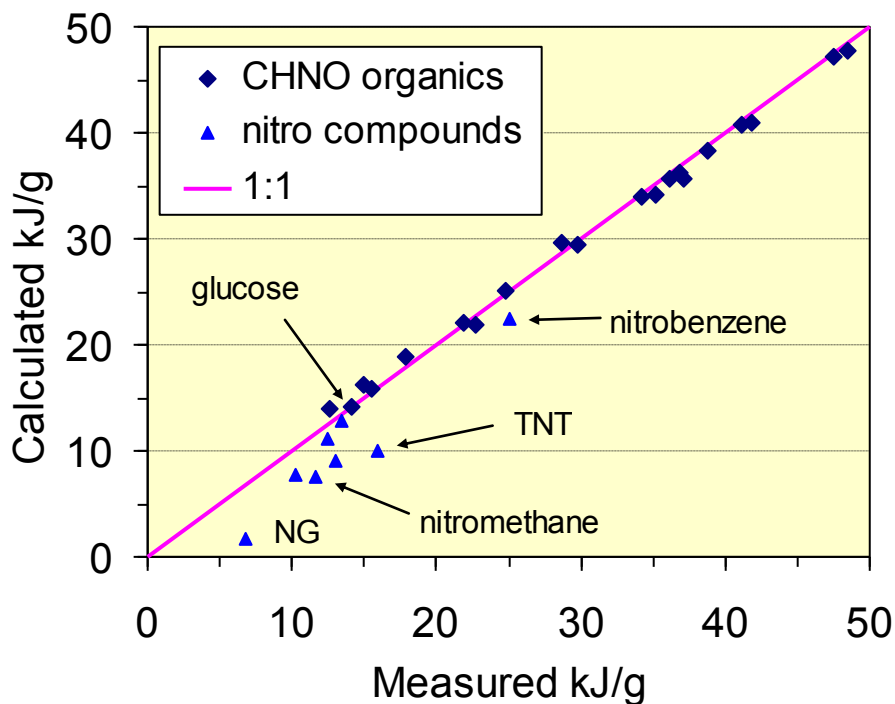
$$-\Delta H_c = 347.3 * \text{wt\% C} + 1151 * \text{wt\% H} + 29 * \text{wt\% N} + 42 * \text{wt\% S} - 108 * \text{wt\% O} \quad (3)$$

The values of the C, H, and N coefficients are in between those of the Boie and Dulong equations. The oxygen coefficient is more similar to that in the Boie equation. The sulfur coefficient is lower than in either equation and is based on matching the trends in heats of combustion reported for amino acids.<sup>5</sup> Sulfur content is so low in food, however, that it has a negligible effect on the final result.

**Table 1.** Comparison of three simple equations for calculating the heat of combustion of oil shale kerogen and food components.

|              | C<br>wt% | H<br>wt% | N<br>wt% | O<br>wt% | S<br>wt% | Boie<br>kJ/g | Dulong<br>kJ/g | Burnham<br>kJ/g | Measured<br>kJ/g |
|--------------|----------|----------|----------|----------|----------|--------------|----------------|-----------------|------------------|
| kerogen      | 80.5     | 10.3     | 2.4      | 5.75     | 1.05     | 38.0         | 41.0           | 39.5            | 39.9             |
| lipid        | 77.1     | 11.9     |          | 11.0     |          | 37.8         | 41.3           | 39.5            | 39.3             |
| protein      | 53.1     | 6.8      | 15.9     | 23.4     | 0.8      | 23.9         | 23.7           | 24.3            | 23.8             |
| carbohydrate | 44.4     | 6.2      |          | 49.4     |          | 16.3         | 15.0           | 17.2            | 17.6             |

Eq. 3 was also compared to the heat of combustion of twenty organic compounds of varying C, H, N, and O composition, ranging from normal alkanes to alcohols to amino acids, taken from the 63<sup>rd</sup> CRC Handbook. The agreement is very good, as shown in Figure 1. The standard deviation is 0.77 kJ/g, or 2.7% of the mean. Also shown is a comparison to the heat of combustion of various nitro compounds, and the agreement is not so good. Clearly, the nitro group enthalpy is inconsistent with the compound range of interest and would require either a separate correlation or a correlation that differentiates among various functional groups. This level of detail is outside the scope of the current effort. Also worth noting is that the standard deviation for the food class components is only half as large as for this more diverse set of organic molecules. Further improvements could be made with an appropriately selected calibration set and multiple regression analysis.



**Figure 1.** Comparison measured heats of combustion for common organic chemicals with those calculated using Eq. 3.

### Conversion of Heat of Combustion to Heat of Formation

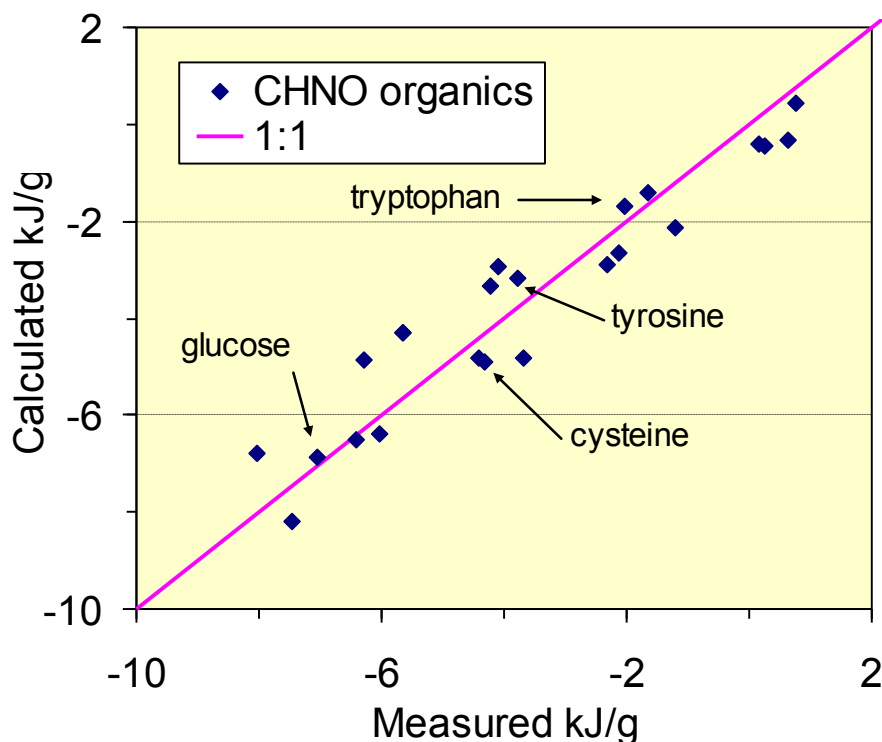
Heats of combustion and formation differ in the point of reference. Heats of formation are with respect to elemental C and sulfur, H<sub>2</sub>, and O<sub>2</sub>, while heats of combustion are with respect to carbon dioxide, water, and sulfur dioxide. Nitrogen has a reference state of N<sub>2</sub> in both cases. If one knows the elemental composition of the material, the heat of combustion is easily converted to the heat of formation by subtracting the heats of combustion of the free elements.

The heats of combustion of C, H<sub>2</sub>, and S are -393.1, -285.8, and -294.3 kJ/mole, respectively (63<sup>rd</sup> CRC Handbook). These correspond to -32.8 kJ/g C, -142.9 kJ/g H, and -9.2 kJ/g S, respectively. These, in turn, correspond to adjustments of the coefficients of Eqs. 1-3 by -327.6, -1429.2, and -92.0 J/g per wt% C, H, and S, respectively. Consequently, an equation for the heat of formation of a “typical” organic compound in foodstuff or biomass is

$$\Delta H_f = 19.7 \cdot \text{wt\% C} - 278.2 \cdot \text{wt\% H} + 29 \cdot \text{wt\% N} - 50 \cdot \text{wt\% S} - 108 \cdot \text{wt\% O} \quad (4)$$

Note that the sign of this equation is switched, since the heat of combustion is the heat of the products (CO<sub>2</sub> and water) minus the heat of formation of the starting materials. This sign makes sense, because a more exothermic heat of formation related to higher oxygen content in the starting material reduces the heat of combustion. The heats of formation calculated by this formula are compared in Figure 2 to heats of formation for 22 CHNO

compounds and one CHNSO compound (cysteine) taken from Lange's Handbook of Chemistry (12<sup>th</sup> edition). The standard deviation between measured and calculated heats of formation is 0.85 kJ/g, which is about equal to that for the heats of combustion. Note that the list of compounds used in this comparison is similar to but not identical to the heat of combustion comparison, because not all compounds were available in both lists. It is reasonable to expect that standard error for estimating food components is only about 0.4 kJ/g, based on both the errors associated with glucose and the amino acids in Figure 2 and the smaller deviation mentioned earlier for the heats of combustion.



**Figure 2.** Comparison of measured heats of formation for 23 organic compounds with that calculated from Eq. 4.

### Measured Heats of Combustion of Materials of Interest

Larry Thorne of Sandia has acquired measured heats of combustion and elemental analysis for nine foodstuffs of interest from an outside laboratory. These provide an opportunity to test the equations developed above. This comparison is given in Table 2. Both the measured and calculated heats of combustion are on a moisture-free basis. “Other” is commonly counted as ash, and the values reported here are similar to ash reported on the USDA web site.<sup>6</sup> For example, USDA ash is 7.6 wt% for cumin, 4.3 wt% for black pepper, and 0.5-1.7 wt% for various flours. “Other” would also include sulfur, but sulfur is estimated to be at most 0.3 wt% for cumin based on protein content (~10× lower than nitrogen content). The standard error of the calculated heats is 0.54 kJ/g, or 2.7%. The calculated heats are systematically higher than the measured values by 1.9%. Correcting for this bias, the random error is 0.38 kJ/mol.

**Table 2.** Comparison of measured heats of combustion with that calculated from elemental analysis. The elemental analyses and measured values come from Larry Thorne at Sandia. The C, H, N, and O percentages are on an as-received basis, except H and O from moisture has been subtracted from the H and O values. The heats of combustion, both measured and calculated, are reported on a moisture-free basis, i.e., divided by (1-wt fr H<sub>2</sub>O).

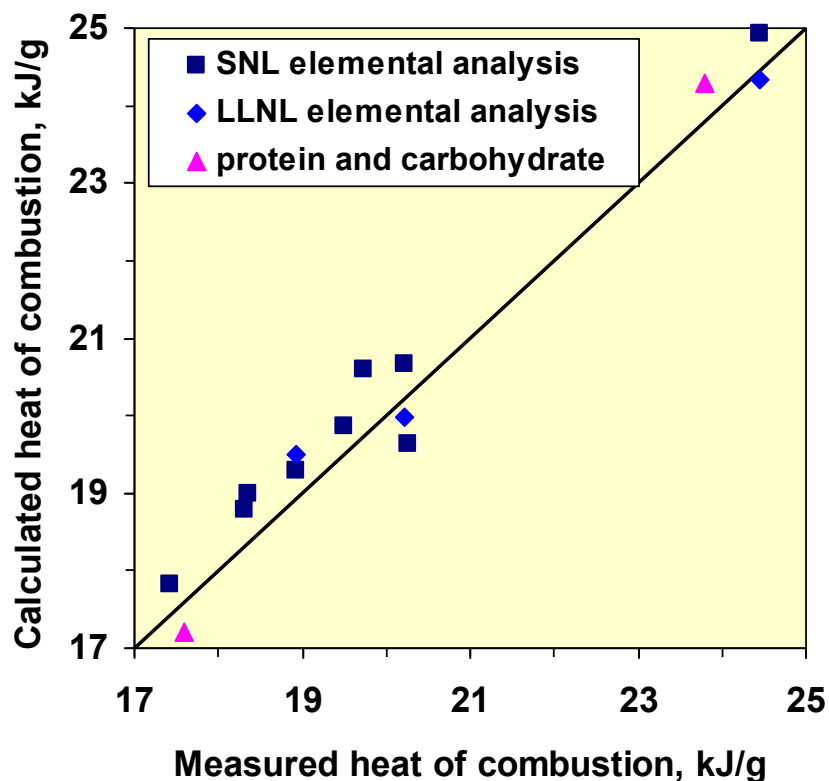
| Food           | C<br>wt% | H<br>wt% | N<br>wt% | O<br>wt% | Other<br>wt% | Moisture<br>wt% | Meas.<br>kJ/g | Calc.<br>kJ/g |
|----------------|----------|----------|----------|----------|--------------|-----------------|---------------|---------------|
| Cotton         | 42.49    | 5.89     | <0.50    | 43.37    | 2.87         | 5.38            | 17.424        | 17.81         |
| Cumin          | 50.07    | 6.70     | 3.15     | 23.85    | 6.95         | 9.28            | 24.455        | 24.93         |
| Semolina flour | 39.81    | 5.66     | 2.13     | 35.68    | 3.83         | 12.89           | 18.354        | 19.00         |
| Black pepper   | 44.89    | 5.58     | 2.03     | 32.36    | 5.00         | 10.14           | 20.216        | 20.67         |
| White flour    | 40.43    | 5.71     | 2.01     | 38.00    | 2.04         | 11.81           | 18.317        | 18.79         |
| Atta flour     | 42.10    | 5.85     | 2.65     | 34.40    | 4.17         | 10.83           | 19.495        | 19.87         |
| Chapatti flour | 41.21    | 5.75     | 2.66     | 35.41    | 4.00         | 10.97           | 18.921        | 19.30         |
| Pine shaving   | 46.97    | 5.66     | < 0.5    | 35.58    | 4.07         | 7.72            | 19.737        | 20.57         |
| Cedar shavings | 46.10    | 4.62     | < 0.5    | 34.07    | 5.13         | 10.08           | 20.251        | 19.63         |

It is interesting to see the differences in different materials. The higher heat of combustion of cumin can be traced to its higher lipid content, which is typical of seeds. The USDA web site reports 22.3 wt% lipid content in cumin. Red pepper and acorn flour also have high lipid content, so they would be expected to have high heats of combustion.

Elemental analyses of some foods used in LLNL experiments were also obtained at LLNL. These results are shown in Table 3. The C, H, and N are reported on an as-received weight basis but do not include contributions from moisture, sulfur is estimated from nitrogen content and other information, and oxygen is estimated by difference. Moisture and ash are measured by TGA for the cumin samples and from the USDA tables and Table 2 for flour and black pepper. For comparison, USDA reports 8.1 wt% moisture and 7.6 wt% ash in cumin. Heats of combustion calculated from the LLNL elemental analyses are also shown in Table 3 on both a dry and dry, ash-free basis. The calculated heats agree very well with the experimental values in Table 2, even though there are minor differences between the elemental analyses between Table 2 and Table 3. A summary of the three sets of calculations for energy of foodstuffs and biomass is shown in Figure 3. The overall trend is calculated very well.

**Table 3.** Calculated heats of combustion (moisture-free bases) for four foodstuffs used in LLNL experiments. C, H, N, O, S values are given on an as-received basis. O is by difference and does not include moisture.

|                | C<br>wt% | H<br>wt% | N<br>wt% | O<br>wt% | S<br>wt% | TGA<br>moisture | TGA<br>ash | Calc.<br>kJ/g |
|----------------|----------|----------|----------|----------|----------|-----------------|------------|---------------|
| Cumin1         | 49.81    | 7.07     | 3.52     | 26.64    | 0.3      | 6               | 6.7        | 24.13         |
| Cumin2         | 50.30    | 7.11     | 3.43     | 27.36    | 0.3      | 7               | 4.5        | 24.53         |
| Chapatti Flour | 41.08    | 6.39     | 2.42     | 38.01    | 0.1      | 10              | 1.6        | 19.50         |
| Black pepper   | 44.19    | 5.77     | 2.12     | 37.02    | 0.2      | 9               | 2.7        | 19.97         |



**Figure 3.** Summary of calculated versus measured energies of foodstuffs and biomass. Lipids are not shown, because they are more energetic by more than the entire range shown here.

### Heats of formation of foodstuffs and biomass

The ultimate goal of this exercise is to supply heats of formation for energetics calculations. The most accurate way, in principle, is to use the experimental values. However, the approach developed in this report enables one to calculate them from elemental analysis alone. One should remember that the elemental composition needs to be measured regardless of whether one has an experimental heat of combustion, because the correction for standard states depends on the elemental composition.

Calculated heats of formation are given in Table 4 along with the experimental heats of combustion. In units of J/g, they are calculated from the experimental value by the simple formula

$$-\Delta H_f = \Delta H_c + 327.4 \cdot \text{wt\% C} + 1429.2 \cdot \text{wt\% H} \quad (5)$$

Sulfur contributions are neglected. A sulfur content of 0.2 wt% would increase the heat of formation by 0.018 kJ/g.

The heats of formation are reported on two bases: as received (wet), and dry. For the as-received basis, the hydrogen content of the water is added to that reported in Table 2. For the dry basis, the carbon and hydrogen wt% values were renormalized to the dry basis. The heats of formation are similar for the two approaches, but those on the dry basis are less exothermic by about 1 kJ/g. The enthalpy of formation of water is -15.88 kJ/g, which is about three times that of the organics. If present at 10 wt%, it would be expected to increase the average by 27%, which is close to the ~1 kJ/g observed.

The heats of formation are also calculated directly from elemental composition using Eq. 4. These values are similar to that calculated by adjusting the experimental heat of combustion but are systematically less exothermic by about 0.5 kJ/mol, which as expected based on the systematic error for calculating the heat of combustion.

An additional observation is that Eq. 4 was derived for organics, not hydrogen. If one uses it to calculate the heat of combustion of a stoichiometric mixture of H<sub>2</sub> and O<sub>2</sub> (11.1 wt% H and 88.9 wt% O), one obtains -12.69 kJ/g, which is 20% lower than the experimental value. Therefore, it is recommended that Eq. 4 is used for calculating heats of combustion of dry foodstuff and biomass and that moisture be added separately and explicitly to any energetic calculation.

A final comment is that most organics contain a few to nearly 10% ash, which is composed of various metal oxides, carbonates, and possibly sulfates. The actual chemical form in the original foodstuff or biomass is different. This is problematic when attempting to construct an empirical formula for the original material. My calculations all assume it is an inert diluent.

**Table 4.** Estimated heats of formation for materials of interest on wet and dry bases.

| Material       | Wet $\Delta H_c$<br>meas.<br>kJ/g | Wet $\Delta H_f$<br>Eq. 5<br>kJ/g | Wet $\Delta H_f$<br>Eq. 4<br>kJ/g | Dry $\Delta H_c$<br>meas.<br>kJ/g | Dry $\Delta H_f$<br>Eq. 5<br>kJ/g | Dry $\Delta H_f$<br>Eq. 4<br>kJ/g |
|----------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| Cotton         | -16.486                           | -6.701                            | -6.167                            | -17.424                           | -6.174                            | -5.797                            |
| Cumin          | -22.186                           | -5.255                            | -4.538                            | -24.455                           | -4.170                            | -3.706                            |
| Semolina flour | -15.989                           | -7.178                            | -6.216                            | -18.354                           | -5.895                            | -5.260                            |
| Black pepper   | -18.167                           | -6.120                            | -5.390                            | -20.216                           | -5.014                            | -4.567                            |
| White flour    | -16.153                           | -7.117                            | -6.335                            | -18.317                           | -5.946                            | -5.486                            |
| Atta flour     | -17.383                           | -6.476                            | -5.809                            | -19.495                           | -5.339                            | -4.975                            |
| Chapatti flour | -16.845                           | -6.609                            | -5.926                            | -18.921                           | -5.464                            | -5.094                            |
| Pine shaving   | -18.212                           | -6.520                            | -5.471                            | -19.737                           | -5.693                            | -4.868                            |
| Cedar shavings | -18.210                           | -5.740                            | -5.335                            | -20.251                           | -3.877                            | -4.511                            |

Another basis that might be used is the dry, ash-free basis. In this case, the elemental composition is renormalized so that all measured elements, CHNO in this case, add to 100%. Those renormalized weight percentages are shown in Table 5. Also shown is the measured heat of combustion adjusted to the ash-free basis, a value calculated using Eq. 3, and heats of formation calculated from Eqs. 4 and 5. These elemental composition can be renormalized to an empirical formula and the heats of formation converted to a molar basis for input to energetics models. However, any application of this species would have to add the ash and water as specific components of the mixture for accurate calculations.

**Table 5.** Measured and calculated heats of combustion and formation on a dry, ash-free basis.

| Food           | C<br>wt% | H<br>wt% | N<br>wt% | O<br>wt% | Meas.<br>H <sub>c</sub> kJ/g | Eq. 3<br>kJ/g | Eq. 5<br>kJ/g | Eq. 4<br>kJ/g |
|----------------|----------|----------|----------|----------|------------------------------|---------------|---------------|---------------|
| Cotton         | 46.31    | 6.42     | 0.00     | 47.27    | -17.94                       | -18.37        | -6.91         | -5.98         |
| Cumin          | 59.77    | 8.00     | 3.76     | 28.47    | -26.28                       | -27.00        | -6.54         | -4.01         |
| Semolina flour | 47.80    | 6.80     | 2.56     | 42.84    | -19.08                       | -19.87        | -7.01         | -5.50         |
| Black pepper   | 52.90    | 6.58     | 2.39     | 38.13    | -21.28                       | -21.89        | -6.50         | -4.84         |
| White flour    | 46.93    | 6.63     | 2.33     | 44.11    | -18.70                       | -19.23        | -6.52         | -5.62         |
| Atta flour     | 49.53    | 6.88     | 3.12     | 40.47    | -20.34                       | -20.84        | -6.56         | -5.22         |
| Chapatti flour | 48.47    | 6.76     | 3.13     | 41.64    | -19.71                       | -20.21        | -6.61         | -5.33         |
| Pine shaving   | 53.25    | 6.42     | 0.00     | 40.34    | -20.57                       | -21.52        | -6.87         | -5.09         |
| Cedar shavings | 54.37    | 5.45     | 0.00     | 40.18    | -21.35                       | -20.81        | -5.34         | -4.78         |

## Summary

The energy content of foods and biomass is consistent and predictable from its elemental composition. The higher the oxygen content of the material, the more exothermic the heat of formation. The lower the oxygen content, the higher the carbon plus hydrogen content, which means a more exothermic state once all material is oxidized.

Correlations developed for estimating the heat of combustion of fossil fuels work reasonably well for foods and cellulose-rich biomass, but they can be improved by slight modification of the elemental coefficients. One such modified equation is presented, and it predicts the heats of combustion of food components and cellulose to about 0.5 kJ/g. It also does well with a broader range of organic chemicals.

The heat of formation of foods and biomass can be estimated from the heats of combustion by changing the reference state from CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub> to C, H<sub>2</sub>, and S. This approach can be used for either developing an equation for estimating the heat of formation of an organic compound or material from its elemental composition or for converting the experimental heat of combustion to the heat of formation. An equation for estimating the heat of formation of organic matter was developed in this manner, and its standard deviation was about the same as for the heat of combustion correlation from which it was derived.

Potentially more accurate estimations of the heat of formation are possible from the measured heat of combustion. The primary issue here keeping track of what basis is used (as received, dry, or dry-ash-free), since water and ash act as energy diluents. Substantial errors will be introduced in subsequent energetics calculations if an inconsistent basis is used.

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